

Fundamentals of Organic and Biochemistry

Miriam Malm

Fundamentals of Organic and Biochemistry

Miriam Malm

The University of New Mexico

D. Van Nostrand Company

New York

Cincinnati

Toronto

London

Melbourne

D. Van Nostrand Company Regional Offices:
New York Cincinnati

D. Van Nostrand Company International Offices:
London Toronto Melbourne

Copyright © 1980 by Litton Educational Publishing, Inc.

Library of Congress Catalog Card Number: 79-91776
ISBN: 0-442-26234-5

All rights reserved. No part of this work covered by the copyright hereon may be reproduced or used in any form or by any means—graphic, electronic, or mechanical, including photocopying, recording, taping, or information storage and retrieval systems—without written permission of the publisher. Manufactured in the United States of America.

Published by D. Van Nostrand Company
135 West 50th Street, New York, N.Y. 10020

10 9 8 7 6 5 4 3 2 1

PREFACE

Fundamentals of Organic and Biochemistry is primarily for students in allied health areas, such as nursing, dental hygiene, nutrition, and physical therapy. The book is also suitable for students in other fields that require a knowledge of organic and biochemistry. The prerequisite for the material is one semester of general chemistry.

This book was written in the firm belief that a fresh approach was needed to meet the needs of students in the allied health areas. The writing style is concise, simple, and "to the point." The content is of a practical rather than theoretical nature. The book is divided into two major parts, each consisting of seven units. Part 1 deals with organic chemistry, Part 2, with biochemistry. The material is organized in a logical manner combining the organic topics with the biochemistry wherever possible to make a cohesive whole.

Part 1 emphasizes mastering the nomenclature and characteristic physical and chemical properties of the principal organic families. For the part, only chemical reactions that will also be encountered in the biochemistry part are included. Thus students studying a complex biochemical family will already have considerable knowledge of these substances from their organic study.

Part 2 gives students a substantial insight into the structure and properties of complex biomolecules, such as carbohydrates, lipids, proteins, hormones, and enzymes. Of particular importance is the function and utilization of these substances. The final unit deals with metabolism. It is a fitting culmination for all previous material and leaves students with a practical and comprehensive understanding of and appreciation for the chemical complexity of the living organism.

The book has been thoroughly tested by several hundred students during its development at the University of New Mexico, and the material reflects their suggestions and responses. Student reaction to the textbook content and style has been highly favorable.

The general design of the book facilitates self-teaching. Short exercises with answers immediately follow new topics. This procedure gives students

the opportunity to test themselves on new concepts while they are still very fresh in their minds. Progress Checks are given at the end of each unit and answers are provided at the back of the book. Students can test themselves to determine whether they have successfully assimilated the material before they proceed to the next unit. Learning Goals in the form of questions precede each unit. As a further test after completing a unit, students can refer to these questions.

The book is adaptable to different academic programs. The materials can be covered in a four-credit one-semester lecture course or in a two-quarter course. For shorter programs, such as the three-credit one-semester course, selected topics can be omitted (or used as suggested reading), thereby retaining the key topics generally required in a text of this level. Selected topics for omission are outlined in the Instructor's Manual or they can be selected at the discretion of the instructor.

The Instructor's Manual includes a list of suggested topics for omission for the shorter academic programs, a sample quiz for each unit (some questions may have to be omitted for the shorter programs), and two two-hour examinations covering each of the two major portions of the text, organic chemistry and biochemistry.

Finally, to those teachers who elect to adopt this book for their students, I would sincerely appreciate their suggestions and comments.

I would like to acknowledge the following reviewers for their helpful comments: Jerome Bigelow, Idaho State University; David Dever, Macon Junior College; Barbara Frohardt, Oakland Community College; John Vosbigian, Los Angeles Harbor College.

My grateful thanks are extended to the many students who used the material in this book during its development. Special thanks go to those students who voluntarily evaluated the material and reported errors and inconsistencies or who made valuable suggestions for improvement. To all of these students, this book is dedicated.

Miriam Malm

CONTENTS

Part 1 Fundamentals of Organic Chemistry

UNIT 1:	BECOMING FAMILIAR WITH ORGANIC COMPOUNDS	3
	1.1 Organic Chemistry—A Major Chemical Branch	3
	1.2 Basic Differences Between Organic and Inorganic Compounds	6
	1.3 Properties of Organic Versus Inorganic Substances	9
	1.4 Carbon, Covalency, and Structural Formulas	11
UNIT 2:	A CLOSER LOOK AT COVALENT BONDING, CARBON, AND CARBON COMPOUNDS	18
	2.1 Review of Covalent Bonding and Covalent Molecules	18
	2.2 Formation and Properties of Some Single Covalent Bonds	19
	2.3 Carbon—Hydrogen Compounds with Single Covalent Bonds Only	22
	2.4 Molecular Formulas, Structural Formulas, Structural isomerism	29
	2.5 Naming the Alkane Hydrocarbons	35
	2.6 Principal Classes of Organic Compounds (Names and Characteristic Functional Groups)	42
	2.7 Kinds of Structural isomerism	45
UNIT 3:	PHYSICAL PROPERTIES OF ORGANIC COMPOUNDS: MORE ABOUT THE HYDROCARBONS	51
	3.1 Intermolecular Attraction and Physical Properties	51
	3.2 Trends in Physical Properties within Classes	57
	3.3 Some Other Physical Properties of Organic Compounds	58
	3.4 Classes of Hydrocarbons	59
	3.5 The Alkenes. Formation and geometry of the Carbon—Carbon Double Bond	60
	3.6 Structural and Geometric Isomerism	62
	3.7 Naming Alkenes	66
	3.8 Properties of the Aliphatic Alkanes and Alkenes	69

3.9	Benzene and Aromatic Compounds	76
3.10	Properties of Benzene and Benzene Derivatives	82

UNIT 4: ORGANIC COMPOUNDS POSSESSING OXYGEN WITH SINGLE BONDS: THE ALCOHOLS, ETHERS, AND PHENOLS 91

4.1	The Alcohols	91
4.2	The Ethers	103
4.3	The Phenols	107

UNIT 5: ORGANIC COMPOUNDS POSSESSING NITROGEN AND SULFUR: THE AMINES, THIOLS, AND SULFIDES 111

5.1	The Amines and Amine Salts	111
5.2	Properties of Amines and Amine Salts	114
5.3	Review of Acidity and Basicity: Hydrogen Ion Concentration and the pH Scale	120
5.4	Some Special Compounds which Contain N and Have Basic Properties	124
5.5	Sulfur-Containing Compounds	126
5.6	Special Organic Compounds which Possess Sulfur	128

UNIT 6: COMPOUNDS WITH A CARBON—OXYGEN DOUBLE BOND: THE CARBONYL COMPOUNDS 133

6.1	The Carbonyl Functional Group. Classes of Carbonyl Compounds	133
6.2	Naming Aldehydes, Ketones, and Carboxylic Acids	134
6.3	Properties of Aldehydes and Ketones	138
6.4	Carboxylic Acids	144
6.5	Salts of Carboxylic Acids	147
6.6	Esters and Amides	149
6.7	Special Esters and Amides	160

UNIT 7: STEREOISOMERISM AND OPTICAL ACTIVITY: THINKING IN THREE DIMENSIONS 171

• 7.1	Review of Conformation and Isomerism	171
7.2	What is Stereoisomerism?	172
7.3	What is Chirality?	173
7.4	Molecules Having One Chiral Center	174
7.5	Enantiomers	175
7.6	Polarized Light and Optical Activity	179
7.7	Assignment of Configuration	181
7.8	Examples of Biochemically Important Compounds with Chiral Centers	182
7.9	Compounds with Two or More Chiral Centers	183
7.10	Molecules with Similar Chiral Centers. The Meso Isomer	185

Part 2 Fundamentals of Biochemistry

UNIT 8:	THE CARBOHYDRATES: OUR SOURCE OF ENERGY	194
8.1	What are Carbohydrates?	194
8.2	Classification of the Carbohydrates (Saccharides)	196
8.3	The Monosaccharides	96
8.4	Assignment of Configuration	199
8.5	Mutarotation and the Cyclic Forms of the Monosaccharides	202
8.6	Properties of the Monosaccharides	207
8.7	Important Disaccharides—Structure and Properties	209
8.8	Important Polysaccharides—Structure and Properties	213
8.9	Special Carbohydrates	216
UNIT 9:	THE LIPIDS: NATURE'S WATER REPELLANTS	220
9.1	What are the Lipids?	220
9.2	The Fatty Acid Lipids (FA Lipids)	221
9.3	The Waxes	227
9.4	The Triacylglycerols—The Storage Lipids	228
9.5	How Soaps and Synthetic Detergents Work	230
9.6	Fate of Ingested Fats and Oils	232
9.7	Special Reactions of Fats and Oils	232
9.8	The Membrane or Structural Lipids	234
9.9	The Phosphoacylglycerols (Phosphoglycerides, Glycerol Phosphatides)	235
9.10	The Sphingolipids	238
9.11	Structure of Membranes and Membrane Transport	239
9.12	Prostaglandins	240
9.13	The Isoprenoid Lipids (Non-Saponifiable)	242
UNIT 10:	THE PROTEINS: THE BASIS OF LIFE	249
10.1	What are the Proteins?	250
10.2	The <i>alpha</i> -Amino Acids (α -AA)	251
10.3	Properties of the L- <i>alpha</i> -Amino Acids	256
10.4	Formation and Hydrolysis of Peptides	259
10.5	Some Important Naturally Occurring Peptides	266
10.6	The Proteins	267
10.7	Primary, Secondary, and Tertiary Structure of Protein	267
10.8	Nature of AA's in Fibrous and Globular Protein	272
10.9	Quaternary Structure of Proteins	272
10.10	More About Fibrous Proteins	273
10.11	More About Globular Proteins	274
10.12	General Chemical Properties of Proteins	275

10.13	Fate of Ingested Protein	276
10.14	Essential Amino Acids	278

UNIT 11: BODY FLUIDS AND TRANSPORT: BLOOD—THE VITAL FLUID 282

11.1	Nature and Function of Body Fluids	282
11.2	Water—The Ideal Physiological Fluid	283
11.3	Digestion, Absorption, and Transport	285
11.4	Osmosis and Dialysis	290
11.5	Regulation of Fluid Exchange	291
11.6	Fluid Volume and Electrolyte Balance	293
11.7	Upsets in O.P. Relationships and Fluid Exchange (Shock and Edema)	294
11.8	Upsets in Normal Blood Pressure	295
11.9	The Principal Components of Blood and Their Functions	298
11.10	Regulation of Blood pH	300
11.11	The Chemistry of Respiration	301
11.12	Abnormal Conditions	303
11.13	The Oxygen Transporters	305
11.14	Hemostasis and Blood Clotting	307
11.15	Degradation of Hemoglobin	310

UNIT 12: ENERGY AND BIOCHEMICAL REACTIONS: ATP AND ENERGY FLOW 315

12.1	Energy and Some Thermodynamic Principles	315
12.2	Energy and Living Systems	318
12.3	Adenosine Triphosphate (ATP) and Metabolism	318
12.4	Introduction to the Nucleotides	321
12.5	Structure of ATP and the High Energy Bonds	323
12.6	Energy "Flow" via Coupling	325
12.7	Activation Energy Barrier and Catalysts	325

UNIT 13: BIOCHEMICAL CATALYSTS AND REGULATORS: THE ENZYMES, HORMONES, AND PROSTAGLANDINS 330

13.1	The Enzymes	330
13.2	Structures and Functions of the B Vitamins	333
13.3	Size and Conformation of Enzymes. Theory of Enzyme Action	339
13.4	Specificity of Enzymes	342
13.5	Enzymes Function at Mild Conditions by Lowering E_{act}	343
13.6	Speed of Enzyme-Catalyzed Reactions	343
13.7	Enzyme Kinetics and the Michaelis-Menten Equation	344
13.8	Regulation of Enzyme-Catalyzed Reactions by Enzyme Control	346
13.9	Feedback Inhibition	346
13.10	Enzyme Inhibition by External Agents	347

13.11	Zymogen Activation	350
13.12	Isozymes (Isoenzymes)	351
13.13	Serum Enzymes as Diagnostic Tools	351
13.14	The Hormones—Secretion, General Function, and Chemical Composition	353
13.15	Other Important Chemical Messengers	356
13.16	Interaction of Hormones, c-AMP, PG's, and Enzymes	358

UNIT 14:	METABOLISM: PRODUCTION OF ATP AND SYNTHESIS OF PROTEIN	364
14.1	Overview of Previous Material	365
14.2	Scope of this Unit	366
14.3	The Cell Sites of Metabolic Processes	367
14.4	Interrelation of Metabolic Processes	369
14.5	Glycolysis and ATP Production (Glucose to Lactate)	370
14.6	Fate of Lactate. Conversion to Acetyl Coenzyme A and the "Shuttle"	373
14.7	The Aerobic Pathway of ATP Production (Cellular Respiration)	375
14.8	The Fatty Acid Cycle and ATP Production	383
14.9	More About Acetyl CoA	386
14.10	Regulation of Blood Glucose	390
14.11	Lack of Effective Insulin and Diabetes Mellitus	392
14.12	Nitrogen Metabolism	393
14.13	The Nucleic Acids—The Chemistry of Heredity	396
14.14	Theory of Replication	399
14.15	The Biosynthesis of Protein	400
14.16	Enzyme Repression and Induction	405
14.17	Defective DNA and Genetic Disease	406
	BIBLIOGRAPHY	412
	PROGRESS CHECK ANSWER KEYS	413
	INDEX	428
	FLOW CHART OF FUNCTIONAL GROUPS AND INTERRELATED REACTIONS	437
	PERIODIC CLASSIFICATION OF THE ELEMENTS	438

**Fundamentals
of
Organic
Chemistry**

PART

1

BECOMING FAMILIAR WITH ORGANIC COMPOUNDS

1

LEARNING GOALS

- What is organic chemistry? How is it related to other areas of chemistry?
- What is the origin of the term “organic”?
- How could organic chemistry be more accurately named?
- What kind of substances are organic? What are sources of organic compounds?
- Why is a knowledge of organic chemistry valuable?
- Why are organic substances usually classified and studied separately from inorganic substances? How do these two classes generally differ?
- Why is carbon considered a special element? In what ways can carbon bond to other atoms?
- What is meant by “covalency”? What is a structural formula? What does a structural formula tell us that a molecular formula does not?

1.1 ORGANIC CHEMISTRY—A MAJOR CHEMICAL BRANCH

Chemistry, broadly speaking, is the physical science that deals with the composition and properties of matter. Matter is *anything* which has mass and occupies space. Organic chemistry is a major branch of this vast science.

Major Branches of Chemistry

- | | |
|------------------------|----------------------|
| • Analytical Chemistry | • Organic Chemistry |
| • Biochemistry | • Physical Chemistry |
| • Inorganic Chemistry | |

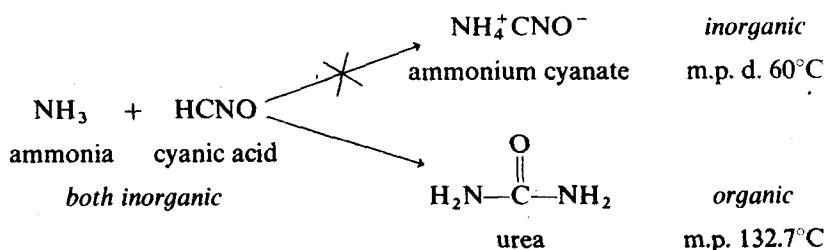
Each major branch may be divided into sublevels. Biochemistry, which has been considered a sublevel of organic chemistry, is now assuming major status in its own right. Medicinal chemistry and the chemistry of natural products are sublevels of organic chemistry, but they may also be considered as "overlap" areas of organic chemistry and biochemistry. Much overlap occurs between the major branches. Qualitative organic chemistry, which deals with the composition of organic substances, overlaps organic and analytical chemistry.

"Organic"—A Misnomer

The term "organic" is actually inaccurate but remains due to usage over the years. Before the middle 1800's chemists believed that organic substances could originate only from living or organic matter, plants and animals. They believed that this kind of matter possessed some "vital force" necessary for its formation because no one had succeeded in making an organic substance in the laboratory from inorganic or mineral sources. Hence the chemistry dealing with such substances was named **organic chemistry**.

The first evidence to disprove this "vital force" theory appeared in 1828 under accidental circumstances. Friedrich Wöhler, a German chemist, was attempting to make ammonium cyanate in his laboratory by heating a mixture of ammonia and cyanic acid. The white crystalline product he obtained possessed the same kinds and numbers of atoms as ammonium cyanate. However, Wöhler found the product to have different properties, and consequently he concluded that it must be a different substance. The product was identified as **urea**, an organic compound. Urea is a major component of urine and is the means whereby nitrogen not needed by the human body is excreted.

Note that in the following diagram urea has a melting point of 132.7°C, while ammonium cyanate melts with decomposition at 60°C. The fact that these two substances have different melting points is evidence that they are two different compounds.

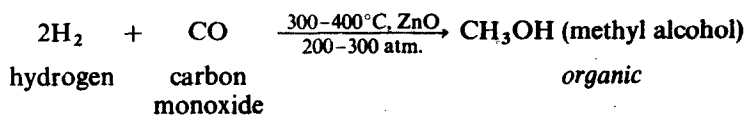


A number of years later and after other organic compounds had been synthesized from inorganic sources, scientific thinking was reversed and

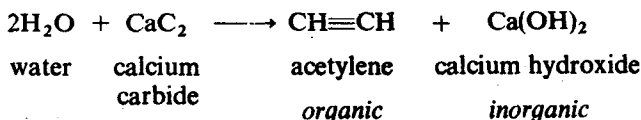
the "vital force" theory was finally discarded. The importance of the accidental synthesis of urea by Wöhler lies in the fact that an important breakthrough in scientific thinking resulted. Actually the synthesis of organic compounds from inorganic material is restricted to a limited number of small, structurally simple organic molecules and is by no means a general method of production.

Two other examples of the synthesis of an organic compound from inorganic sources are:

1. The industrial production of methyl alcohol from hydrogen and carbon monoxide using heat, high pressure, and a catalyst.



2. The reaction between water and calcium carbide to produce acetylene, a gas used in welding torches.



Carbon in Organic Compounds

If "organic" is not an accurate title for this important branch of chemistry, what would be better? It is known that all organic compounds possess one particular element, the element **carbon**. They can have from one carbon, as urea or natural gas (methane, CH_4), to thousands of carbon atoms as some complex protein molecules. A more accurate title therefore could be the *Chemistry of Compounds of Carbon*.

Occurrence and Sources of Organic Compounds

We are composed of and surrounded by a myriad of different organic substances. Within us are hormones, enzymes, proteins, and genes, to name just a few. The clothes we wear—cotton, silk, polyester—and the foods we eat containing sugars, fats, proteins, and vitamins are organic. Most drugs, detergents, and insecticides are organic. Plastics, paint, paper are organic. Automobile tires, vinyl seat covers, and the gasoline and oil consumed by our automobiles are organic substances. All of these substances are put together in a special way to give them their various properties and uses.

Today most organic compounds are *synthesized* in the laboratory from other organic compounds. Over a million organic compounds have been synthesized with perhaps many more millions to come in the future.

A principal *natural* source are the *fossil fuels*, petroleum and coal, which result from the decay of living matter over milleniums of time. From the relatively simple components of petroleum and coal many more complex compounds have been made.

A second natural source of organic compounds are *living* plants and animals. The food we eat contains carbohydrates, fats, proteins, and vitamins obtained from living matter. Many drugs are derived from natural substances: morphine used to relieve pain is obtained from the oriental poppy; the antibiotic streptomycin is a product of certain soil micro-organisms; insulin, used to control diabetes mellitus, is extracted from the pancreas of sheep.

**Knowledge of
Organic
Chemistry—A
Valuable Asset**

Everyone can benefit from a knowledge of organic chemistry. We find ourselves in an era of technology where pollution is endangering our environment. Problems such as drug abuse have become of world-wide concern. Under such conditions, maintaining good health and seeking the prevention and cure of disease are of prime concern to us all. As a direct result of these problems, research is being conducted at an unprecedented rate to untangle the mysteries of life. The genetic code has been broken; the memory code is in the process of being broken. The mechanism of hormone action is slowly becoming known. Chemistry lies at the very *core* of these endeavors.

It follows that persons employed directly in the various health sciences must have a sound knowledge of organic chemistry and biochemistry. But persons not in these areas can benefit also. Ask yourself these questions. Should not a parent understand the potential hazards of insecticides stored in the garage, cleansing agents stored under the kitchen sink, or drugs stored in the bathroom cabinet? Should not a teacher or employer be able to recognize signs of illness or drug abuse in the classroom, office, or factory?

1.2 BASIC DIFFERENCES BETWEEN ORGANIC AND INORGANIC COMPOUNDS

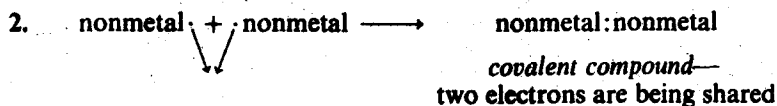
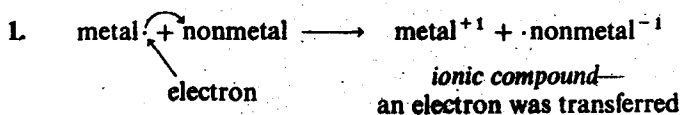
Because organic compounds differ from inorganic compounds in striking ways, the two groups are usually classified and studied separately. Three fundamental differences among the two classes are:

1. the *kinds of elements* composing the groups
2. the type of *chemical bonding* between the atoms
3. the *shape and size* of the composite particles

Organic compounds are composed of a small number of nonmetals. Only trace amounts of various metals occur. Inorganic compounds are composed of a great assortment of both metals and nonmetals. The following nonmetals commonly occur in organic compounds.

- *Carbon* is always present.
- *Hydrogen* is almost always present (an exception is CCl_4 —carbon tetrachloride).
- *Oxygen* and *nitrogen* are frequently present.
- *Sulfur* and *phosphorus* are present to a lesser degree than O or P.
- *Halogens* (F, Cl, Br, and I) are present frequently, but usually only in synthetic organic compounds. An exception is iodine which is a component of thyroxine, the thyroid hormone.

Remember from beginning chemistry that atoms can chemically combine in one of two ways: 1) by the transfer of electrons to form ions, or 2) by the sharing of electrons to form molecules. The attraction between oppositely charged ions constitutes an *ionic bond*; metals combine with nonmetals in this way. Two nonmetals bond to each other by the formation of a *covalent bond* in which they share a pair of electrons. The resultant compounds are called **ionic** and **covalent** compounds, respectively.



Covalent compounds exist as neutral molecules. Ionic compounds are aggregates of oppositely charged ions held in position by strong electrostatic attraction. Forces exist between molecules, but they are not nearly as strong as ionic attraction.

